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XII.

CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.

ON THE OCCLUSION OF GASES BY THE OXIDES OF METALS.

By Theodore William Richards and Elliot Folger Rogers.

Presented May 10, 1893.

In the course of an investigation upon the atomic weight of copper, recently conducted in this Laboratory, it was noted that cupric oxide prepared by the ignition of the nitrate always contains a considerable amount of occluded gas, which is composed mainly of nitrogen.* Cupric oxide prepared from the carbonate, on the other hand, appears to possess no such property of occluding gases. Since the material used by Hampe and others had all been made by the former method, it was at once evident that the occluded gas contained in the oxide was wholly responsible for the formerly accepted erroneous results for the atomic weight of copper.

The results of these experiments suggested the possibility that gases might be occluded by all oxides prepared in this way from the nitrates. It became a matter of much importance to test the point, for such oxides have often furnished the starting point for determinations of atomic weights.

The method adopted in the present research was precisely similar to that used in the case of the cupric oxide. Since it is by no means certain that indefinite heating in a vacuum could drive out all the gas from the compact, often crystalline compound under examination, the material was dissolved in acids under such conditions that the gas set free could be measured and analyzed.

The simple apparatus needed has been described and explained in the paper already quoted. The material to be investigated was placed in the largest bulb of the bulb-tube shown in the accompanying diagram, and the tube was about half filled with cold water which had been thoroughly boiled. The whole was then connected with the water pump, and freed from adhering air bubbles by agitation in the partial vacuum, — the water being allowed to boil gently under the reduced pressure. Subsequently, the tube was filled with boiled water, and returned to its normal horizontal position. Pure acid was now run in from a pipette, a short piece of glass rod within the large bulb furnishing a means of agitating the oxide during its solution. The gas which was set free was finally collected and measured in the sealed end of the apparatus. In the concluding experiments, where greater accuracy was desired, the gas was transferred, and remeasured in a tube which had been carefully calibrated by means of mercury.

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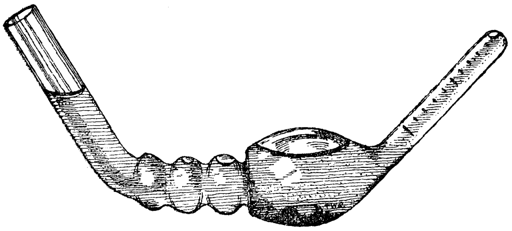
* Theodore W. Richards, These Proceedings, XXVI. 281. In 1868 Frank land and Armstrong pointed out this fact; but their statement lacked definiteness, and has since been largely forgotten.



The gas was analyzed with the help of a small Hempel's apparatus made for the purpose. The burette with which the first ten analyses were made was about seven millimeters in internal diameter and could be read to a fiftieth of a cubic centimeter, while that used for the later analyses was only four millimeters in diameter and could be read with reasonable certainty to the hundredth. The portion of the gas absorbed by caustic potash was assumed to be carbon dioxide, and the further portion which was absorbed by alkaline pyrogallol was assumed in like manner to be oxygen. The residue was perfectly inert, and was undoubtedly nitrogen. One sample of this residue obtained from zincic oxide, was mixed with oxygen and subjected to the spark of an induction coil, without diminution in volume. The apparatus and chemicals were tested from time to time by analyses of air.

In every case, the gas while saturated with aqueous vapor was measured at the ordinary temperature and atmospheric pressure of the room. The variations from the mean values of 22° and 76.0 centimeters were not sufficient to need attention in crude work of this kind, when working upon such very small quantities of gas.

Zincic Oxide.

Preliminary experiments with this substance gave results exactly corresponding to those obtained from cupric oxide. If the substance was prepared by ignition of the nitrate, very considerable amounts of gas were found to be occluded; while material of a similar grade of purity in every other respect made by heating zincic carbonate appeared to contain no trace of gas.

The oxide used in the first three experiments was made by treating so called pure zinc with nitric acid, evaporating to dryness, redissolving the zincic nitrate in water with the addition of a little nitric acid, precipitating a small amount of iron with ammonia in slight excess, evaporating the filtrate, and igniting the residue. This gave a faintly yellow oxide.

For the second series, a nearly neutral solution of fairly pure zincic chloride was precipitated while boiling by a solution of sodic carbonate. Part of the basic carbonate thus formed was ignited directly, the oxide thus produced containing no occluded gas (Experiment 4). The remainder was dissolved in nitric acid, evaporated to dryness, and ignited to the full heat of the blast lamp in an open porcelain crucible. Experiments 5, 6, and 7 are analyses of this yellowish sample.

For the third series a solution of "chemically pure" zincic nitrate was allowed to stand over an excess of zinc for some time. The filtered solution was evaporated until a portion of the nitrate had been converted into the basic salt. The whole was then poured into distilled water, and a solution of normal nitrate was thus obtained after the basic salt had been filtered off. This solution was treated a number of times with zincic hydrate, — which had been precipitated by ammonia and washed until free from the salts of this base, — and allowed to stand. The filtered solution was evaporated to dryness and heated in a porcelain crucible to about 240° C. over a ring burner. Part of this was analyzed at once (Experiment 8), part heated by a Bunsen burner (Experiments 9 and 10), and part ignited at a very high temperature in a Hempel clay furnace with the blast lamp and bellows (Experiments 11 and 12). Experiment 13 was made with a soft white oxide prepared from the basic nitrate.

Analyses 14 to 27 inclusive were made from oxide obtained as follows. Pure white zincic oxide of commerce was dissolved in nitric acid, and carefully washed zincic carbonate was added to this solution in slight excess. The whole was allowed to stand with occasional shaking for some time, and finally filtered and evaporated rapidly by boiling. This gave a sample of the oxide which was very nearly white after intense heating in a double porcelain crucible.

In Experiments 22 and 23, pure oxygen was introduced into the flame of the blast lamp used for igniting the zincic oxide, the bottom of the outer crucible being melted where the flame struck it. The material analyzed in Experiment 22 was taken from the layer nearest to the zincic silicate formed in the bottom of the crucible by fusion of the glaze, and that used in Experiment 23 was taken from the top. The zincic oxide of Experiment 24 was heated to bright yellow heat in the same way. All the edges of the porcelain were rounded, and the cover and the crucible itself were fused to the heavy iron supports on which they rested. After twelve minutes the iron itself began to burn and the ignition was stopped. The oxide was found to be " sintered together," and was of a grayish color, as if it had been reduced in part. The inference was corroborated by the presence of zincic oxide on the cover of the crucible and on the sides of the stack of the furnace. The zincic oxide used in Experiment 25 was treated in a similar manner, but proved to be still darker in color. It was afterwards ignited for some time in an atmosphere of oxygen, in order that no reduced metal might be left.

The materials used in Experiments 26 and 27 were separate samples heated in a double crucible, with the cover of the inner crucible fitting inside the outer one, instead of covering both. This arrangement rendered less likely the entrance of reducing gases, and allowed freer play of air in the furnace. After the latter had been thoroughly heated by the ordinary blast lamp, oxygen was slowly turned on through a Y tube, to replace a large part of the air in the flame. This gave an intense white heat, which melted and burned the tip of a file in the fraction of a minute. In Experiment 27 the glaze of the inner crucible was fused, and the platinum which separated the two crucibles was cemented to the outer crucible. The crystalline residue of zincic oxide after this treatment was white with the faintest trace of yellow, but no sign of gray. As the crucible would not stand a higher heat, and as any quantitative determination could scarcely be carried on at a higher temperature, no attempt was made to push the heat further.

The fifth series of determinations was made with the object of discovering whether the trace of silica and alkali dissolved from the glass and porcelain might be responsible for the occlusion of the gases. First, a sample of the purest zinc that could be obtained was treated with a small amount of pure nitric acid in a porcelain dish, and the solution evaporated to small bulk in the presence of an excess of zinc.

Upon dilution the basic nitrate, which contained most of the impurities not deposited upon the zinc, was precipitated and removed by filtration. The solution was then evaporated to dryness and the residue ignited in porcelain. (See Experiments 28 and 29.) Another sample of zinc was dissolved in a similar way in platinum, and the resulting solution of the pure nitrate was divided into several portions. One portion was evaporated in glass and ignited in porcelain, the residue containing somewhat more gas than that which had been treated wholly in porcelain. (See Experiments 30, 31, 32, and 33.) Another part was evaporated and ignited in platinum (Experiment 34). This sample was undoubtedly reduced in part by the diffusion of gases from the flame.* Still another portion was ignited for a short time only in platinum, the ignition being completed in porcelain (Experiment 35). A fourth portion was ignited for a short time in an open platinum dish with free access of air (Experiment 36). Finally, the remainder of the solution of pure zincic nitrate was evaporated and ignited in a platinum vessel enclosed within one of porcelain. This specimen was not exposed to the action of reducing gases, and upon solution it evolved almost exactly the same amount of gas as the specimen which had been prepared in glass and ignited in porcelain. (See Experiments 37 and 38.)

Experiment 39, using zincic oxide prepared from the carbonate, was made to test again the accuracy of the method.

The weight of zincic oxide taken for each individual experiment is tabulated in the second column of the following table, and the third column indicates approximately the conditions used for the ignition of the different portions. The volume of gas given off on the subsequent solution of the zincic oxide in sulphuric acid is recorded in the fourth column, while the fifth contains the same data reduced to the standard of ten grams of zincic oxide. The sixth column contains a record of the analyses of the gases, and the seventh supplies information upon a few minor points connected with individual results.

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* Erdmann, Pogg. Annal., LXII. 611. Morse and Burton, Am. Chem. Journ., X. 311-321.

No. of Exp.	Weight of Zincic Oxide.	Time and Temperature of Heating.	Volume of Gas evolved.	Volume of Gas calc. for 10 gr. of ZnO.	Analysis of Gas by Volume.	Remarks.
	grams.		c.c.	c.c.		
1	1.375	Blast lamp	1.6	12.0		
2	1.19	"	1.45	12.2		
3	1.225	"	1.53	12.5		
4	1.1	"	0.00	00.0		From carbonate.
5	1.05	"	2.1	20.	$CO_2 = 2.0\%$ $O_2 = 55.5$ $N_2 = 42.5$	
6	1.08	"	2.1	19.4		
7	1.075	"	2.15	20.		
8	1.27	240° C.	0.00	00.0		Gave test for nitrates.
9	1.005	Bunsen flame	.70	7.0		
10	1.065	"	.78	7.3		
11	1.22	Blast lamp Hempel furnace	.58	4.7		
12	1.91	"	.92	4.8		
13	1.05	Water blast Hempel furnace	.20	1.9		Made from basic nitrate.
14	1.07	Water blast furnace 30 min.	.75	7.0		Fourth Series.
15	1.00	"	.71	7.1		
16	1.02	Blast	1.52	14.9	$CO_2 = 1.3\%$ $O_2 = 53.8$ $N_2 = 44.8$	
17	1.10	Water blast Furnace 2 hr.	.35	3.2	$O_2 = 9.1$ $N_2 = 90.9$	Partly reduced.
18	1.20	" 3½ "	1.12	9.1		18–21 heated in double crucible by water blast in furnace. Samples removed from time to time.
19	1.06	" 5 "	.83	7.8		
20	.85	" 6 "	.46	5.4		
21	.92	" 6½ "	.53	5.8		
22	1.07	Furnace 6½ hr. Oxygen flame, 15 min.	.42	3.9	$CO_2 = 0.0\%$ $O_2 = 16.9$ $N_2 = 83.1$	Layer next the silicate.
23	1.125	The same.	.48	4.3		Upper layer.

No. of Exp.	Weight of Zincic Oxide.	Time and Temperature of Heating.	Volume of Gas evolved.	Volume of Gas Calc. for 10 gr. of ZnO.	Analysis of Gas by Volume.	Remarks.
	grams.		c.c.	c.c.		
24	1.03	Oxy. fl. 15 min.	.24	2.3	$O_2 = 16.7\%$ $N_2 = 83.3$	Partially reduced and reoxidized.
25	1.105	" 30 "	.19	1.7		Reduced more than Ex. 24 and reoxid
26	.72	White heat 20 min.	.33	4.6	$CO_2 = 0$ $O_2 = 24\%$ $N_2 = 76$	White after ignition.
27	1.0125	White heat 35 min.	.45	4.4		" "
28	1.05	Water blast ½ hr.	.42	4.0		Fifth Series.
29	1.019	" 1½ "	.37	3 6		
30	1.34	Bunsen Flame 30 min.	.28	2.10		Probably contained nitric acid.
31	1.05	Water blast 30 min.	.97	9.2		
32	1.0035	Water blast 1 hr.	.68	6.8		
33	.9765	1½ hr.	.63	6.4		
34	1.03	Water blast ½ hr.	.175	1.7		Partially reduced.
35	1.08	½ hr.	.35	3.2		Less reduced.
36	1.50	20 min.	.82	5.46		Possibly reduced in part.
37	1.004	1½ hr.	.68	6.8		
38	1.018	2 hr.	.68	6.7		
39	1.00		0.00	0.00		Prepared from carbonate.

It is evident that we are dealing here with a phenomenon similar both qualitatively and quantitatively to that observed in the case of copper. Zincic oxide prepared from the nitrate occludes a very appreciable quantity of nitrogen and a somewhat variable quantity of oxygen. Continued application of heat tends to drive out both gases, the oxygen being less firmly held than the nitrogen; but the highest heat which we were able to obtain was insufficient wholly to eliminate either gas. Under like conditions, specimens of zincic oxide made from zincic nitrate which had been obtained in a number of different ways appeared to hold approximately the same amounts of gas. It is almost, if not quite, impossible to prepare the oxide in this manner in a state wholly free from solid impurities taken from the containing vessel during the ignition of the purest possible zincic nitrate. The effort was made in the preceding series of analyses to prepare samples which must contain wholly different kinds of impurities. The fact that these different samples contained almost equal amounts of gas shows with reasonable certainty that the impurities are not responsible for the occlusion.

It is noticeable that the oxide obtained at a very low temperature, which still contained traces of zincic nitrate, contained little or no occluded gas (Experiments 8 and 30) ; also that six specimens which had been suspected of partial reduction contained much less gas than similar material free from this suspicion (Experiments 17, 24, 25, 34, 35, and 36).

Nickelous Oxide.

The series of experiments with nickelous oxide led to results not unlike those with zincic oxide. In this case sulphuric acid proved unsatisfactory as a solvent, and hydrochloric acid was adopted. A solution containing about twenty per cent of hydrochloric acid gas was freed from air by continued boiling, rapidly cooled, and run into the tube containing the oxide of nickel. On account of the very slow action of the cold acid the tube was warmed after exhausting the air as usual. The gas set free was measured as before.

In order to prove the accuracy of the method a gram of zincic oxide prepared from the carbonate was dissolved in hot hydrochloric acid in precisely a similar way. No trace of gas was evolved during this solution.

It was thought unnecessary to make a series of experiments as elaborate as that made with the zincic oxide. Nickelous nitrate was evaporated to dryness in porcelain and ignited fifteen minutes in a blast lamp and then a number of hours over a Bunsen burner in the furnace. (Analysis 1, below.)

A part of the nickelous oxide remaining was further ignited for two hours in the furnace by means of the water blast. This was used for the second analysis. A portion of the latter was ignited again in the furnace at the highest temperature we could obtain, by the addition of oxygen to the flame for about fifteen minutes, until the bottom of the outer crucible as well as the platinum foil between the two crucibles was melted away. The arrangement of data in the table is similar to that already described.

No. of Exp.	Weight of Oxide.	Volume of Gas evolved.	Volume of Gas calc. for 10 gr. NiO.	Analysis of Gas by Volume.
	grams.	c. c.	c. c.	Per Cent.
1	1.14	.469	4.11	O_2 = 12.25 N_2 = 87.75
2	.997	.34	3.41	
3	1.13	.35	3.09	O_2 = 8.8 N_2 = 81.2

MAGNESIC OXIDE.

The experiments with the oxide of magnesium led to very unexpected results, the amount of gas evolved upon the solution of this compound being five to twenty times as much as was obtained from zincic oxide, and over twenty-five times as much as from the oxide of nickel. More difficulty was found in decomposing the nitrate than before, and the remaining oxide was in a much harder and more compact state, and consequently more difficult to pulverize. The process used was similar to that employed in the case of the other oxides.

Magnesic nitrate made from pure nitric acid and magnesic carbonate of commerce was evaporated to dryness in porcelain. The residue was pulverized in an agate mortar, heated by means of the blast lamp in a covered porcelain crucible, and cooled over calcic chloride. For a parallel experiment, a portion of the original carbonate was converted into the oxide by simple ignition, the magnesia formed in this way evolving only an extremely small amount of gas upon solution (Experiment 2 below).

A third portion of magnesic nitrate was made from pure magnesium ribbon and pure nitric acid, and the oxide was obtained from this salt by evaporation and ignition in porcelain as usual (Experiment 7).

Sulphuric acid was used for the solution of the magnesic oxide, as in the case of zincic and cupric oxides. The following table explains itself.

No. of Exp.	Weight of Oxide used.	Temperature and Time of Heating.	Volume of Gas evolved.	Volume of Gas calc. for 10 gr. of MgO.	Analysis of Gas.	Remarks.
	grams.					
1	.50	Blast lamp, 30 min.	5.45	109.	O_2 = 66.6% N_2 = 33.4	
2	about 1.0	" 1 hr.	.05	.5		Made from carbonate.
3	.50	" 1¼ hr.	5.86	117.2	CO_2 = 5.98 O_2 = 53.7 N_2 = 40.29	Analyses made from one sample of oxide heated under different conditions. 1, 3, & 4 gave tests for nitrates with ferrous sulphate; 5 & 6 did not.
4	.25	" 2¼ hr.	2.31	92.4	O_2 = 47.6 N_2 = 52.4	
5	.25	" 3¼ hr.	2.31	92.4	CO_2 = 2.2 O_2 = 38.9 N_2 = 58.9	
6	.25	Oxygen blast, 20 min.	2.04	81.6	O_2 = 34.3 N_2 = 64.2 CO_2 = 1.5	
7	.25	Water blast, 1½ hr.	2.31	92.4		

The amount of gas occluded by magnesic oxide is thus far more than that occluded by the oxides of copper, zinc, and nickel. The quantities of carbon dioxide recorded in the table are undoubtedly far from accurate, since the gas was collected over water. It is interesting to note that the amount of nitrogen evolved by the oxide upon going into solution was slightly increased up to a certain point by the increasing time and heat of the ignition, while the amount of oxygen was rapidly diminished.

No. of Exp.	Volume of Nitrogen found in 1 gram of MgO.	No. of Exp.	Volume of Oxygen found in 1 gram of MgO.
	c.c. Gas.		c. Gas.
1	3.6	1	7.2
3	4.72	3	6.3
4	4.84	4	4.4
5	5.44	5	3.6
6	5.24	6	2.8

The Oxides of Cadmium, Mercury, Lead, and Bismuth.

These oxides, the only other suspected ones which could be easily analyzed by the method in hand, all yielded negative results. The oxide of cadmium was distinctly crystalline, and contained only the merest trace of gas. The oxides of mercury, lead, and bismuth obtained by the ignition of the corresponding nitrates also appeared to contain no occluded gaseous impurity.

Unfortunately, the oxides of antimony, iron, and a number of other metals, are not sufficiently soluble in acids to test with ease their power of occlusion by this method. It seems probable that interesting results might be obtained from them: hence in the near future other methods will be tried here, with the hope of determining if these oxides also occlude gaseous impurity.

Theoretical Considerations.

From the fact, observed with both copper and zinc, that oxides which still contain a trace of nitrates, as well as those made from the carbonate, retain no imprisoned gas, it is readily inferred that the decomposition of a trace of nitric acid is alone responsible for the impurity. It is natural that this last trace of nitric acid should be confined below the surface, whence the gases resulting from its ultimate decomposition would find it hard to escape. On this supposition it is not unnatural that zincic oxide which has been partly reduced, and hence somewhat disintegrated, should contain less occluded gas than that which has not been thus reduced. Moreover, since magnesic nitrate is harder to decompose than the other nitrates, and the oxide is more compact, we should expect to find more gas occluded in this case than in the others. All these inferences agree with the facts. The difference in the rate of expulsion of the oxygen and of the nitrogen is interesting, and less easy to explain.

The negative results observed with a number of metals lead one to conclude that the physical condition of the oxides in these cases was so porous that even the last traces of nitrogen were allowed to escape. Indeed, cupric and zincic oxide made from very finely divided basic nitrates, obtained from aqueous solution, contained much less gas than samples which were obtained in a more compact condition by the direct ignition of the normal nitrate. This fact shows how much depends upon physical conditions.

It must be borne in mind that the occlusion of gases noted in this paper is a very different phenomenon from the retention of undecomposed oxides of nitrogen alluded to by Marignac,* Morse and Burton, and others. Nitrogen present in the state of gas could of course give no test with sulphanilic acid and naphthylamine, or any other test for oxidized nitrogen. It is evident that the phenomenon we are now studying, like the other just spoken of, may be a very serious cause of error in many of the published determinations of atomic weights; these would hence appear lower than their true value, because of the extra material which is calculated as oxygen.† Before any quantitative results obtained in this way can be accepted as authoritative, definite proof must be brought forward of the absence of this source of error. It is to be hoped that the able experimenters who have recently worked upon zinc, nickel, magnesium, and similar metals, have preserved typical specimens of their final products. If this is the case, nothing could be easier than to determine the amount of occluded gas, if any is present, and to apply the necessary correction.

As long ago as 1887 one of us was engaged, through the suggestion of Professor Cooke, upon an investigation of the atomic weight of zinc depending upon the analysis of zincic bromide. The work was discontinued because of the many publications upon this subject which appeared before it could be completed. Since the results recorded in this paper appear to indicate that the last word has not yet been said upon the subject, the investigation of zincic bromide and chloride is now being continued in this Laboratory.

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* "Il est probable que l'oxyde de zinc et la magnésie ne sont pas les seuls oxydes qui retiennent aussi énergiquement des composés nitreux, lorsqu'on les prépare par la calcination de leurs azotates." — Annales de Chemie et de Physique, Series [6], Vol. I. p. 311, foot-note.

† The following are the metals whose atomic weights have been determined by means of the oxide made through action of nitric acid: Hydrogen (cupric oxide), Magnesium, Aluminium, Vanadium, Manganese, Nickel, Cobalt, Copper, Zinc, Gallium, Selenium, Tin, Antimony, Tellurium. See Meyer and Seubert, Atomgewichte, pp. 17 to 42. Also Nickel, Krüss, Z. anorg. Chem., II. 235. Zinc, Morse and Burton, Amer. Chem. Journ., X. 311-321. Magnesium, Burton and Vorse, Chem. News, LXII. 267.